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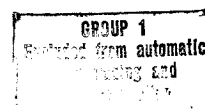ON THE THEORY OF SIMULTANEOUS DISCHARGE

OF METAL IONS IN REAL CONJUGATED SYSTEMS

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ABSTRACT

More satisfactory mathematical relationships are developed
for the speed of discharge of individual metals in alloy
deposition as related to electrode potential and the depolar-
izing effect of the deposit, or the lack of such an effect.
The experimental results with nickel-cobalt and nickel-iron
deposition are discussed, and show that the theory of real
conjugated systems which is presented takes into consider-
ation the regularities of the codischarge of metal ions more
correctly than previous theories.

The concept [1] that in the simultaneous reduction of the ions of metals, the speed of their discharge does not vary with electrode potential in comparison with separate reduction, is the basis of the existing theory.

The available experimental material[2], however, proves that electrochemical reactions of simultaneous discharge of ions are in most cases conjugated ones, i.e. their speeds differ considerably from that at which separate reduction of the ions occurs. It is desirable therefore to distinguish the regularities of two cases of codischarge:

1) Simultaneous discharge in ideal unconjugated systems in which speeds of ions being coreduced do not depend on each other, and are defined by the laws of electrodeposition of the components when they are reduced separately.

2) Simultaneous discharge in real conjugated systems in which the regularities of the reduction of the ion proceeding from the existing theories of ideal unconjugated systems, are affected by mutual influence of the ions being reduced.

1. Codischarge of ions in ideal unconjugated systems

According to the existing laws of electrode processes[1] a necessary condition for the simultaneous discharge of several types of ions must be the equality of their reduction potentials

$$\varphi_1^o + \frac{RT}{nF} \ell n\, a_1 - \eta_1 = \varphi_2^o + \frac{RT}{nF} \ell n\, a_2 - \eta_2 \quad (1)$$

where $\varphi_1\, \varphi_2\, \eta_1\, \eta_2\, Q_1$ and Q_2 are normal potentials of activity and overvoltage respectively which belong to either type of ions of metals.

The laws of the codischarge of ions are usually represented graphically in the following manner (Fig. 1) where discharge potentials vs. current densities for two types of ions are shown. At a given deposition potential the speed of the ion discharge M_1 is expressed by the line $AO = i_1$, and that of ions M_2 by the line $BO = i_2$. The ratio of the currents used for the reduction of ions M_1 and M_2 is $\dfrac{i_1}{i_2}$.

¶ Proceeding from the theory of slow discharge, O.A. Esin[3] calculates the ratio of speeds of ion discharge, considering that

$$i_1 = K_1 \cdot C_1 \cdot e^{-\frac{\gamma_1 n_1 F \varphi}{RT}} \qquad (2)$$

and

$$i_2 = K_2\, C_2 \cdot e^{-\frac{\gamma_2 n_2 F \varphi}{RT}} \qquad (3)$$

where:

K_1 and K_2 are constants of the speed of electrochemical reactions

C_1 and C_2 are concentrations of ions in the electrolyte;

γ_1 and γ_2 are fractional coefficients;

n_1 and n_2 are valences of ions;

φ is electrode potential.

According to equations (2) and (3) we find

$$\frac{i_1}{i_2} = \frac{K_1 C_1 e^{-\frac{\gamma_1 n_1 F \varphi}{RT}}}{K_2 C_2 e^{-\frac{\gamma_2 n_2 F \varphi}{RT}}} \qquad (4)$$

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V. L. Kheifets and A. L. Rotinyan[4] have developed an analogous equation for the codischarge of ions. In their reasoning these authors proceed from the concept that the nature of the dependance of the speed of separate electrode reactions upon the potential does not change with the coreduction of ions.

2. Codischarge of Ions in Real Conjugated Systems

As has been stated the experimental results of the codischarge of ions do not agree with the above regularities. The existing theories of codischarge do not take into account the fact that the speed of electrode processes during the codischarge of ions varies, depending on the change in the substrate nature, the structure of the double layer, and the state of the ions in the solution, which are different when discharged separately and when codischarged.

Changes of the properties of the electrode surface may be of two kinds: 1) the reduction potential of metal ions may become lower as a result of alloy formation depolarization; 2) the speed of ion reduction may be affected to a certain degree by a change in the substrate nature and by its tendency to passivation (polarization).

Facilitation of the process of reduction of metal ions in the course of alloy formation is connected with the change of partial free energy of the alloy components, and the equilibrium potential of the components shifts to the positive side due to this fact by a value of

$$\Delta \psi = \frac{\overline{\Phi}}{nF} \qquad (5)$$

where: $\Delta \psi$ is the value of the change in the equilibrium

potential at the expense of the energy of com-

ponent interaction with the formation of an alloy;

$\bar{\Phi}$ is the change in partial molar free energy.

It should be noted that the experimental results with re-
gard to the amount of depolarization are complicated by a change
in the state of the electrode surface. Therefore, in most cases
thermodynamic values of the change of free energy during form-
ation in the process of electrodeposition of metals from aqueous
solutions do not agree with the values of depolarization found
experimentally. The higher the overvoltage of metal deposition
the greater this deviation will be.

From the theory of electrode processes it is known that
if the overvoltage is over 25 mv, we have a linear dependency
between the value of overvoltage η and the logarithm of the
current density (i):

$$\eta = a + b \ell n i \tag{6}$$

where the constant $\underline{a}$ depends upon the nature of the metal and
its surface state.

The constant $\underline{a}$ may have various values. For example, dur-
ing hydrogen liberation $\underline{a}$ varies from 1.56 mv for lead to
0.1 - 0.03 for the metals of platinum group. In the codepos-
ition of metals the nature of the electrode substrate will differ
from the substrate when the metals are electrodeposited separately.
Not only chemical but also passivational polarization of the electrode
will change with the change of the substrate nature.

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Hence, the speed of ion reduction during codischarge and separate dischage will naturally be substantially different.

The speed of ion reduction during codischarge will also vary due to the change in the structure and concentration of ions in the electrical double layer. It should be noted that the speed of reduction of ions depends upon their concentration in the electrical double layer, but not upon the concentration in the solution. As is known[5] the ion concentration in the double layer C_s is connected with the concentration in the body of the solution for the simplest cases by the following equation:

$$C_s = C \cdot e^{-\frac{F\psi}{RT}}$$

(7)

It is evident that in the case of the codischarge of ions at a given value of electrode polarization the concentration of each ion type in the double layer is less than in the case of the separate reduction owing to the partial replacement of some ions by others in the double layer. The degree of replacement of ions of one type by the ions of another type, depends upon their nature. As a result of this replacement the concentration of each type of discharging ion in the double layer decreases at a given value of cathodic overvoltage. This results in lowering the speed of reduction of each type of metal ion and, consequently, a difference in the ion discharge speed vs. electrode potential relation during the coreduction in comparison with the separate reduction.

The presence of other ions in the electrolyte will also influence the speed of reduction in connection with the change in the state of ions in the electrolyte and, in particular, with the change of the extent of their hydration. The influence

of hydration on the speed of ion reduction has been discussed in many papers[6].

When determining the conditions of codischarge of ions in real conjugated systems one should take into consideration the fact that when several types of ions enter the double layer, the portion of polarization introduced by each type of ions will be characterized by the portion of ions entering the electrical double layer with respect to the total number of ions affecting polarization. Let us denote the concentration of each type of ions as C_i, /a coefficient characterizing the ability of a given type of ions to penetrate into the electrical double layer as α_i. The decrease of partial polarization at the expense of the entering of other ions into the double layer may be expressed by the following expression: $-\frac{RT}{nF}\ell n\frac{\Sigma\alpha_i C_i}{\alpha_1 C_1}$. The change of discharge speed of different ions will take place in accordance with this expression.

Since equation (1) expressing the condition of codischarge of ions does not take into account the above listed factors, it must be written in the following manner:

$$\varphi_1^0 + \frac{RT}{nF}\ell n\, C_1 - \frac{RT}{nF}\ell n\frac{\Sigma\alpha_i C_i}{\alpha_1 C_1} - \eta_1^{alloy} = \varphi_2^0 - \frac{RT}{nF}\ell n\, C_2 - \frac{RT}{nF}\ell n\frac{\Sigma\alpha_i C_i}{\alpha_2 C_2} - \eta_2^{alloy}$$

OR

$$\varphi_1^0 + \frac{RT}{nF}\ell n\frac{\alpha_1 C_1}{\Sigma\alpha_i C_i}\cdot C_1 - \eta = \varphi_2^0 + \frac{RT}{nF}\ell n\frac{\alpha_2 C_2}{\Sigma\alpha_i C_i}\cdot C_2 - \eta_2^{alloy} \qquad (8)$$

To simplify, one leaves out of consideration the fact that the activity of each type of ion in the mixture will differ from the activity of ions reduced separately.

Equation (8) assumes that normal potentials of metals do not vary substantially if there is no mutual influence of the metals. A method of calculating the depolarizing action of the deposit in equation (1) has already been suggested by A.I.Krasovskii[7].

It follows from the foregoing that the speed of reduction of each type of ion will decrease during codischarge as compared with their separate reduction if the nature of the substrate does not facilitate the speed of discharge of the metal ions.

In the case when there is considerable change in the nature of the substrate and its surface state, one may expect both an incræse and a decrease in the overvoltage of metals in comparison with their separate deposition, i.e. $\eta_1^{alloy} \lessgtr \eta_1$ and $\eta_2^{alloy} \lessgtr \eta_2$. Therefore, it is possible to observe the change of correlation of the speeds of ion reduction with regard to an increase in the concentration of both the more positive and the more negative metal in the alloy; i.e.

$$\frac{i_1}{i_2} \lessgtr 1$$

so if $\eta_1^{alloy} > \eta_2^{alloy}$ and

$$\varphi_1^{o} + \frac{RT}{nF} \ln \frac{\alpha_1 C_1}{\sum \alpha_i C_i} \cdot C_1 - \left(\varphi_2^{o} + \frac{RT}{nF} \ln \frac{\alpha_2 C_2}{\sum \alpha_i C_i} \cdot C_2 \right) < \eta_1^{alloy} - \eta_2^{alloy} \quad (9)$$

the speed of the more negative metal will be higher as compared with less negative metals.

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EXPERIMENTAL

In order to compare the speed of reduction of individual metals with the speed of their codeposition we determined in each case the current used for the reduction of each type of ion, depending on the electrode potential.

The experimental data on the dependance of the speed of the separate reduction of the ions Co^{++} (curve 1) and Ni^{++} (curve 2) and simultaneous deposition (curve 3), on electrode potential are given in Fig. 2. Polarization curves were obtained by a galvanostatic method. The comparison of speeds of ion discharge during co-reduction and separate reduction showed that at a potential of 900 mv the speed of reduction of nickel ions during codeposition is 10.5 times less as compared with its separate deposition. The speed of the discharge for cobalt ions at the potential of 800 mv during codeposition is 16 times less than during separate deposition. At higher potentials the speed of discharge of cobalt ions in the absence of nickel is much higher and cannot be compared with the speed of discharge of Co^{++} ions when discharged together with Ni^{++} as illustrated in Fig 2.

The delay of the discharge of metal ions during the codeposition can also be observed when the speeds of discharge of ions are studied by a potentiostatic method. During the electrodeposition of cobalt the addition of nickel sulphate to the solution leads to an abrupt decrease in the current used for the discharge of cobalt ions. During the electrodeposition of nickel the addition of cobalt salts does increase the total current flowing through the electrolytic cell, but the current used for the reduction of Ni^{++} ions decreases as

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compared with ~~their~~ separate deposition. The inhibition of the speed of discharge of ions during codeposition may to a considerable extent be connected with a change in the concentration of ions in the electrical double layer.

But these abrupt inhibitions are not only due to the change in the concentration of discharging ions in the double layer. One should also take into consideration the change in the nature of the substrate and the superficial condition of the electrode. Fig. 3 shows the results of the study of separate deposition and code-position of iron and nickel. The curves show that the discharge of nickel ions when codeposited with iron (curve 7) occurs at a much lower speed than when deposition is without iron (curve 4). But the discharge of iron ions when codeposited with nickel (curve 6) proceeds at a higher speed as compared with the deposition of iron only (curve 9). Thus these results clearly show how difficult it is to isolate one component and how easy it is to isolate the other during the codischarge of their ions, in contrast to the separate reduction.

It should be noted that the process of codischarge of metals of the iron group is complicated by the simultaneous discharge of hydrogen ions during both the separate electrodeposition of these metals and their codeposition, which makes it difficult to study the mechanism of this process. Table 1 gives the data on the speeds of reduction of Fe^{++}, Ni^{++} and $H+$ ions, when iron and nickel are deposited both together and separately.

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TABLE I

Distribution of current between certain reactions when the electro-deposition of iron and nickel is carried out both separately and together

Cathode potential = 970 mv

Type of electrode process	SPEED OF ION REDUCTION ma/cm^2			Total speed of electro-process ma/cm^2
	Fe++	H+	NI++	
Electrodeposition Fe without Ni	4.5	4.4		8.9
Electrodeposition Ni without Fe		7.9	20.8	28.7
Electrodeposition Fe together with Ni	13.6	4.5	2.6	20.7

It can be seen from the above data that at a cathode potential of ψ = 970 mv, the speed of discharge of iron ions determined by the current density corresponds to 4.5 ma/cm^2 during separate reduction and to 13.6 ma/cm^2 during coreduction. Thus, when iron is reduced together with nickel the speed of reduction of iron ions becomes three times as high and the speed of the discharge of nickel ions decreases at this potential from 20.8 ma/cm^2 to 2.6 ma/cm^2, i.e. becomes approximately eight times as low. The speed of discharge of hydrogen ions with the simultaneous reduction of nickel is 7.9 ma/cm^2 and that of reduction of hydrogen with iron is 4.4 ma/cm^2, and in the case of codischarge of the ions of nickel and iron it is 4.5 ma/cm^2. From these data it is evident that hydrogen with nickel is isolated at a much higher speed than with iron or during the simultaneous deposition of iron and nickel, which is due to the lower value of

From the analysis of polarization curves and equation 1
it could also be expected according to the theory of simul-
taneous dischage of ions of unconjugated systems that the speeds
of reduction of nickel ions would be higher than those of re-
duction of iron ions, i.e. the amount of nickel in the alloy of
Fe-Ni will be higher than that of iron. The experiemntal data
however resulting from the study of the composition of the alloy
Fe-Ni show the inverse correlation, i.e., the amount of iron in
alloys is higher than that of nickel.

Any deviation from the above regularities can be accounted
for if we assume that the speed of reduction of metal ions changes
abruptly depending on the condition of the electrode surface,
and that passivational polarization during the isolation of the
iron group metals prevails over chemical polarization. The fact
that electrolytic deposits including more foreign particles are
observed with higher overvoltage as compared with lower overvoltage
deposits[8], speaks well for such an assertion. In the case when
nickel is deposited, the deposit contains much more hydroxide
inclusions than hydrogen. In the case of iron deposition the de-
posit contains more hydrogen than hydroxide compounds.[8] It should
be noted that this inhibiting action of adsorbed hydrogen and
hydroxide is also different for each of these metals. When iron
is deposited the speed of reduction of iron ions increases as
the amount of hydrogen evolved decreases, and in the electro-
deposition of nickel the speed of reduction of nickel ions in-
creases as the number of hydroxide inclusions decreases.

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Proceeding from these facts one may assume that an abrupt inhibiting effect on the discharge of iron is due to the adsorption of hydrogen evolved, while the discharge of nickel ions is affected by the adsorption of hydroxide being formed in the layer just at the electrode surface. It is believed that the increase in the speed of reduction of iron ions when coreduction is carried out with nickel is due to the fact that the ability of the alloy Fe-Ni to absorb hydrogen is less as compared with iron. The abrupt delay of the reduction of nickel ions during electrodeposition with iron may be due to the increased adsorption of hydroxide compounds on the surface of the alloy as compared with the separate deposition of the metals, because in the case of iron salts hydroxide formation occurs in a more acid region than in the case of nickel.

Thus one can observe some deviation from the regularities of unconjugated systems due to the different degree of inhibition of metal ions of the iron group when they are reduced together or separately.

It is evident that when the overvoltage in the above case of codeposition becomes considerably low, one can expect a reverse correlation of speeds, i.e., the speed of deposition of the more positive metal (Ni) will be higher than that of the more negative metal (Fe).

With a view to the further discussion of the dependence of overvoltage and composition of the alloy Fe-Ni, we studied the codischarge of ions of nickel and iron. The study was made with 1 N solutions of nickel and iron sulfates with the addition of 30 g/l of boric acid, pH being 1.9, at various temperatures.

Fig. 4 shows the polarization curves of separate discharge and codischarge of the ions of nickel and iron, and also their partial curves obtained with the same solutions at increased temperatures.

It is seen from these curves that in contrast to the curves in Fig. 3, the speed of deposition of nickel in the alloy is higher than that of iron when nickel and iron are electro-deposited at high temperatures.

It is evident that with an increase in temperature and with a decrease in overvoltage in isolating these metals, the speed of reduction of the ions will mainly be defined by the expression:

$$\varphi_1^o + \frac{RT}{nF} \ln \frac{\alpha C}{\sum \alpha_i C_i} C$$

Fig. 5 shows the change in the composition of a nickel and iron alloy during codeposition from the same solutions as a function of the electrolyte temperature. Curve 1 illustrates changes in the percentage content of nickel in the alloy caused by temperature. Curve 2 shows changes in the percentage content of iron caused by temperature.

SUMMARY

These curves show that with an increase in the electrolyte temperature, the speed of reduction of nickel ions increases and that of iron decreases, and at temperatures above 90° C the content of nickel in the alloy becomes larger than that of iron.

Thus, during the simultaneous discharge of two ions, the observed higher speed of reduction of metal ions (Fe^{++}) with a more negative potential of reduction as compared with a less negative metal (Ni^{++}) is connected with changes in overvoltage;

these changes are due to the change in the KXXX nature of the electrode substrate.

The above experimental results show that the theory of real conjugated systems takes into consideration more correctly the regularities of codischarge of metal ions.

CAPTIONS TO FIGURES

Fig. 1.Diagram of electrode potentials versus current densities for metals M_1 and M_2.

Fig. 2. Dependence of speed of reduction of ions of nickel and cobalt en electrode potential, pH = 1.9 and t = 25°C;

1. Discharge of Co^{++} and H+ ions from $2NCoSO_4$.

2. Discharge of Ni++ and H+ ions from 1 N $NiSO_4$;

3. Simultaneous discharge of Ni++, Co++ and H+ ions from solution 1 N in $NiSO_4$ and 2N in $CoSO_4$;

4. Partial curve of discharge of Ni++ ions;

5. Partial curve of discharge of H+ ions;

6. Partial curve of discharge of Ni++ ions;

7. Partial curve of discharge of Co++ ions;

8. Partial curve of discharge of H+ ions.

Fig. 3. Dependence of speed of reduction of ions of iron and nickel on electrode potential, pH = 1.9, t = 25°.

1. Curve for discharge of Ni++ and H+ ions from 1N $NiSO_4$;

2. Curve for discharge of Fe++, Ni++ and H+ ions from solution 1 N in $FeSO_4$ and 1 N in $NiSO_4$;

3. Curve for discharge of Fe++ and H+ ions from 1N $FeSO_4$;

4. Partial curve of discharge of Ni++ ions;

5. Partial curve of discharge of H+ ions;

6. Partial curve for discharge of Fe++ ions;

7. Partial curve for discharge of Ni++ ions;

8. Partial curve for discharge of N+ ions;

9. Partial curve of discharge of Fe++ ions;

10. Partial curve for discharge of H+ ions.

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Fig. 4. Dependence of speed of reduction of iron and nickel ions on electrode potential, pH = 1.9, t = 95°.

1. Curve for discharge of Ni++ and H+ ions from 1 N NiSO$_4$ + 30 g/l of H$_3$BO$_3$;

2. Curve for discharge of Ni++, Fe++ and H+ ions from a solution 1N NiSO$_4$, 1N FeSO$_4$ + 30 g/l of H$_3$BO$_3$;

3. Curve for discharge of Fe++ and H+ ions from 1N FeSO$_4$ + 30 g/l of H$_3$BO$_3$;

4. Partial curve of discharge of Ni++ ions;

5. Partial curve of discharge of H+ ions;

6. Partial curve of discharge of Ni++ ions;

7. Partial curve of discharge of Fe++ ions;

8. Partial curve of discharge of H$^+$ ions;

9. Partial curve of discharge of Fe++ ions;

10. Partial curve of discharge of H+ ions;

Fig. 5. Change in percentage content of iron and nickel in the alloy with temperature. Electrolyte composition: 1N NiSO$_4$, 1N FeSO$_4$ + 30 g/l of H$_3$BO$_3$, pH = 1.9;

Curve 1 - Change in nickel content in alloy;

Curve 2 - Change in iron content in alloy.

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